DECLASSIFIED
DATE 91-8-21
AUTHORIZED BY X HF Sloan

TREATMENT OF URANIUM PROCESS RAFFINATE AT KEY LAKE URANIUM MINES LTD. FOR THE RECOVERY OF NICKEL

G.M. Ritcey, R. Molnar and E.W. Wong

September 1986

Project 30.61.99
Uranium - Cost Recovery

Job No. 025255

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 86-15 (CR)

CONFIDENTIAL

92-02375/

TREATMENT OF URANIUM PROCESS RAFFINATE AT KEY LAKE URANIUM MINES LTD. FOR THE RECOVERY OF NICKEL

by

G.M. Ritcey, R. Molnar and E.W. Wong

ABSTRACT

Investigations were undertaken to recover a Ni by-product from the Key Lake Mining Corp. uranium raffinate solutions. Examination of a number of solvent extraction reagents did not produce acceptable results because of the problem of separating the Ni from the ^{226}Ra. A precipitation flowsheet was devised consisting of oxidation of the raffinate, precipitation of iron and other impurities by neutralization to pH = 3.5, adding $BaCl_2$ to precipitate the ^{226}Ra followed by precipitation of the Ni as a sulphide using Na_2S. Some of the operating parameters were studied with a view to optimization and preliminary reagent cost estimates were made.

2873792 LD

TRAITEMENT D'UN RAFFINAT D'URANIUM À KEY LAKE URANIUM MINES LTD. POUR LA RÉCUPÉRATION DE NICKEL

G.M. Ritcey, R. Molnar et E.W. Wong

RÉSUMÉ

Des études ont été entreprises en vue de récupérer un sous-produit de Ni dans des solutions de raffinat d'uranium de Key lake Mining Corp. L'examen d'un certain nombre de réactifs d'extraction de solvants n'a pas produit de résultats acceptables à cause du problème de séparation du Ni et du ^{226} Ra. Un graphique des étapes suivantes de traitement a été mis au point pour la précipitation : oxydation du raffinat, précipitation du fer et autres impuretés par neutralisation jusqu'à un pH de 3,5, ajout de $BaCl_2$ pour précipiter le ^{226}Ra, puis précipitation du Ni sous forme de sulfure à l'aide de Na_2S. Certains des paramètres d'exploitation ont été examinés en vue d'une optimisation et des estimations préliminaires du coût des réactifs ont été réalisées.

CONTENTS

	ABSTRACT	1
1.	INTRODUCTION	1
2.	FEED SOLUTION AND PROCEDURE	1
3.	SOLVENT EXTRACTION	2
	3.1 Screening Extraction Tests on Various Extractants	2
	3.2 DEHPA + TBP Stripping Test	3
	3.3 DNNSA + LIX 63	5
	3.4 Conclusions on Solvent Extraction	9
4.	PRECIPITATION	9
	4.1 Initial Tests on Synthetic Feed Solutions	9
	4.2 Tests on Key Lake Raffinate - $CaCO_3$ + Na_2S	10
	4.3 Oxidation of Fe^{2+} to Fe^{3+} Followed by $CaCO_3$ and Na_2S Precipitation	11
	4.4 Oxidation - $CaCO_3$ - $BaCl_2$ - Na_2S Precipitation	12
	4.5 Oxidation - $CaCO_3$ Precipitation - Ion Exchange Removal of Radium	15
5.	REAGENT SELECTION AND COSTS	17
6.	DISCUSSION AND CONCLUSIONS	19
7.	RECOMMENDATIONS	22
8.	ACKNOWLEDGEMENTS	22
9.	REFERENCES	22

TABLES

Table 1.	Typical Feed Solution Compositions	2
Table 2.	Screening Tests (Synthetic Raffinate Feed)	3
Table 3.	Preliminary Stripping Tests	5
Table 4.	Screening of Diluents	5
Table 5.	Use of DNNSA as an Extractant	6
Table 6.	Successive Extraction Contacts	7

Table 7. Scrubbing of Loaded Solvent with 100 g/L NaCl 7
Table 8. Effect of Contact Time on Extraction 8
Table 9. Effect of Extractant Mixtures 8
Table 10. Precipitation with Na_2S 10
Table 11. $CaCO_3$-Na_2S Precipitation of Key Lake Raffinate (No pre-oxidation) 11
Table 12. Oxidation - $CaCo_3$-Na_2S Precipitation of Key Lake Raffinate 13
Table 13. Oxidation - $CaCO_3$ + $BaCl_2$ - Na_2S Precipitation 14
Table 14. Oxidation - $CaCO_3$ Pretreatment before IX or Barite Removal of Ra 17

FIGURES

Fig. 1. Nickel Stripping Isotherm 4
Fig. 2. Radium Removal with Barite or by IX 16
Fig. 3. Possible Nickel (Cobalt) Recovery Process from Key Lake Uranium Process Raffinate 21

1. Introduction

The processing of most uranium ores involves the leaching of the crushed and ground ore in a sulphuric acid medium together with an oxidant. This treatment solubilizes the uranium as well as any base metals and some other elements that may be present. At the Key Lake operation in Saskatchewan the ore contains substantial quantities of nickel, arsenic and iron which are solubilized along with the uranium. The uranium is recovered by solvent extraction and the waste raffinate is neutralized, barium chloride added to remove radium, and the clarified effluent discharged to the tailings impoundment area together with the leach solids residue.

The quantity of nickel in solution is substantial, and at a concentration of about 2 g/L Ni is considered to be a potential valuable by-product. Therefore at the request of senior management of Key Lake Mining Corporation made in February 1986, CANMET carried out a project to determine whether a saleable nickel product could be recovered from the uranium process raffinate.

Early in the discussion with Key Lake personnel it was agreed that a bulk nickel concentrate, possibly a mixed Ni-Co sulphide, would be the desired product. Naturally the final product had to be essentially free of ^{226}Ra and it would be desirable to contain as little arsenic as possible. Two process routes were to be considered, one a solvent extraction purification treatment of the raffinate and the other some type of precipitation process.

The bench studies were carried out during the period March-August 1986.

2. Feed Solutions and Procedure

Some initial tests were performed on synthetic feed solutions prior to receiving the actual raffinate from the mill. Various concentrations of solution were prepared to simulate the raffinate liquor composition. The aqueous feed solutions had the compositions shown in Table 1.

Table 1. Typical Feed Solution Compositions
(g/L except Ra in pCi/L)

Synthetic Raffinate Feed		Key Lake Feed Raffinate			
Ni	2.32	Ni	2.06	Mg	0.71
Co	0.046	Co	0.047	Ca	0.67
U	0.095	U	0.0007	Si	0.41
Fe^{3+}	0.5	Ra	5460	Al	1.08
^{226}Ra	1240	Fe_t	2.12	pH	0.95
		Fe^{2+}	1.54		

The sample of as-received Key Lake raffinate contained some white precipitate which was removed before use. This precipitate consisted essentially of gypsum and silica. When the solution was adjusted to pH 4.5 and filtered the dried precipitate analyzed: 7.38% Fe, 7.91% SiO_2, 10.81% Al, 0.95% Ni and 28.17% LOI and 440 pCi/g ^{226}Ra. Prior to contacting the actual feed raffinate with the solvent it was necessary to add 30 ppm Polyox (Union Carbide) followed by filtration in order to obtain a suitable feed to solvent extraction.

All the solvent used in the solvent extraction tests consisted of 5-10% extractant concentration in Varsol 140 diluent. Certain systems had a modifier added. The bench tests were carried out in separatory funnels.

Precipitation tests were usually performed on 1 litre quantities of the feed solution.

3. Solvent Extraction

3.1 Screening of Possible Extractants

Various possible extractants were tested for extraction and separation of nickel from the raffinate. These included the alkylphosphorus acid extractants, carboxylic acid extractants, sulphonic acid and chelating and solvating types (1). The initial tests were performed with the synthetic raffinate feed solution, previously adjusted to pH 3.75 with NaOH and filtered before use. The solvents were all pre-equilibrated with 28% NH_4OH at O/A=16/1. An initial series of tests indicated that no nickel extraction took place without the pre-equilibration step. The use of TBP was instituted because without it the pre-equilibration step produced 3 phases and stable emulsions resulted in extraction. Extraction was at A/O 3/1 for

3 minutes at room temperature. The feed solution, after pH adjustment, contained, in g/L, 2.13 Ni, 0.046 Co, 0.095 U, 0.001 Fe and 1060 pCi/g ^{226}Ra. The results in Table 2 indicate that the DEHPA or PA 216, both alkylphosphorus acids are the best for Ni(Co) extraction. However, considerable ^{226}Ra was also co-extracted.

Table 2. Screening Tests (Synthetic Raffinate Feed)

Reagents	Raffinate (g/L) (pCi/L Ra)					Extraction %	
	Equil. pH	Ni	Co	U	Ra^{226}	Ni	Ra^{226}
10% DEHPA + 5% TBP	6.9	0.43	0.007	0.0004	381	80	64
10% DEHPA	7.3	0.34	0.006	0.0003	369	84	65
10% PA216 + 5% TBP	7.6	0.32	0.006	0.0004	370	85	65
10% LIX 65N	7.7	1.69	0.009	0.0003	980	21	8
10% Versatic 911	7.9	1.10	0.028	<0.0002	1010	48	5
5% DEHPA + 5% TOPO	7.0	1.00	0.013	<0.0002	426	53	60

(Fe <0.0001 g/L for all reagents)

3.2 DEHPA + TBP Stripping Test

The following tests on Key Lake raffinate were performed using the DEHPA + TBP in Varsol 140 solvent mixture. This mixture was selected as typical of the better Ni results of the screening tests with a view to looking for selective stripping possibilities.

Preliminary stripping tests were performed on a solvent loaded with nickel from the synthetic raffinate feed solution to determine the stripping medium if solvent extraction was to be used for nickel recovery. The loaded solvent contained 5.66 g/L Ni and 0.19 g/L Co. Lower concentrations of acid gave satisfactory stripping of Ni but very poor phase separation with emulsion problems. The results in Table 3 indicate 50-100 g/L H_2SO_4 to be the best stripping agent although 1M $(NH_4)_2SO_4$ at pH 1.0 was also effective. The tests were conducted at an A/O ratio of 1/1 with 2 minutes contact at room temperature. A stripping isotherm for Ni using 0.5M $(NH_4)_2SO_4$ at pH 1 is shown in Fig. 1. No selectivity over ^{226}Ra was indicated.

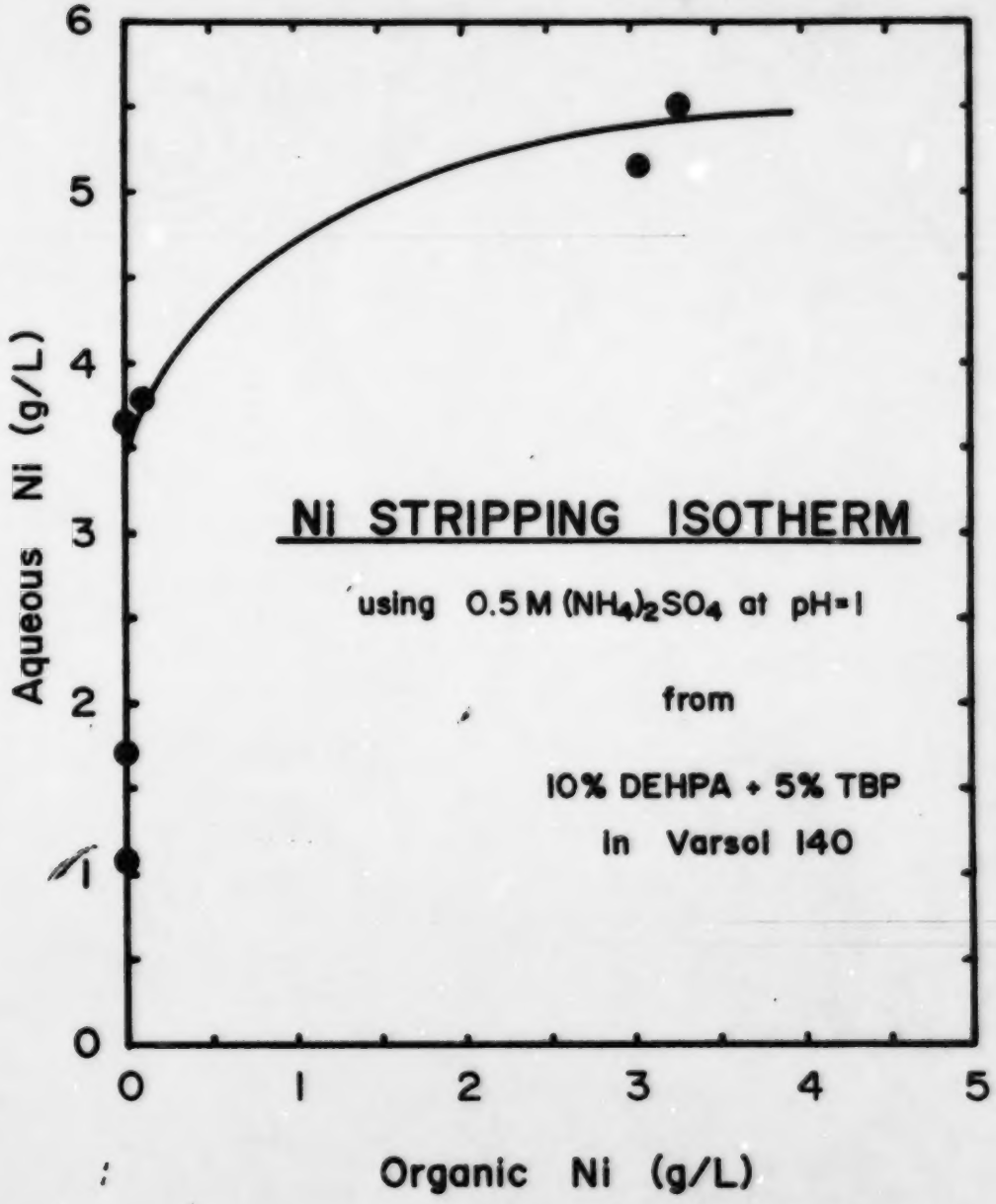

Fig. 1 Nickel Stripping Isotherm

Table 3. Preliminary Stripping Tests

Reagent	Strip Solution (g/L)	
	Ni	Co
H_2SO_4 (pH 1)	1.42	0.025
H_2SO_4 (3M)	4.46	0.12
H_2SO_4 (50 g/L)	4.7	0.14
H_2SO_4 (100 g/L)	4.6	0.13
0.5M $(NH_4)_2SO_4$ (pH 1.0)	3.35	0.13

Concurrent with the examination of the extractants, tests were conducted to determine whether the diluent choice could improve the poor observed phase separation. The solvent composition was 10% DEHPA + 5% TBP in each of several diluents. The extraction was carried out from the synthetic feed at A/O 3/1 for 3 minutes at room temperature with pre-equilibrated (28% NH_4OH at O/A = 16/1) solvent. The qualitative data in Table 4 indicate a wide variation in separation times and clarity of solution with diluent composition.

Table 4. Screening of Diluents

Diluent	Phase Disengagement (seconds)	Remarks	
		Organic	Aqueous
Varsol 140*	55	hazy	cloudy
Solvesso 150	60	hazy	cloudy
Escaid 100	55	hazy	cloudy
Escaid 110	270	clear	clear
Chevron 370	>19 min	clear	clear & interface emulsion
Chevron 425	290	clear	clear
Isopar K	150	clear	clear
Mentor 29	75	hazy	cloudy
Toluene	340	clear	clear

*10% DEHPA, 10% TBP

3.3 DNNSA + LIX 63

Another extractant that was considered as a possibility was dinonylnaphthylsulfonic acid (DNNSA). This reagent was not investigated in the initial tests as it had not been received from the supplier. It is known to extract from acidic medium particularly in mixtures with LIX 63.

Mixtures of DNNSA (acid form and alkali form as a ADNNSA, ammonium) and chelating extracts were investigated. The results are given in Table 5. The extraction was at an A/O ratio of 1/1 for 2 minutes at room temperature. Preliminary tests indicated pre-equilibriation (with acid) was not necessary. The real Key Lake raffinate feed solution to extraction contained 2.05 g/L Ni, 0.048 g/L Co, 2.17 g/L Fe, 0.0008 g/L U and 5920 pCi/g ^{226}Ra.

The mixture of LIX 63 with the sulfonic acid extractant was the best as regarding the most effective nickel extraction. The isotherm for 10% ADNNSA + 15% LIX 63 in contact with Key Lake raffinate feed solution adjusted to pH 1.5-2.0 with NaOH showed a maximum nickel loading of about 1.7 g/L together with 0.45 g/L Fe, 0.046 g/L Co, 0.0008 g/L U and over 10,000 pCi/L ^{226}Ra on the organic.

Table 5. Use of DNNSA as an Extractant

Extractant	pH Feed	Raffinate g/L (pCi/L Ra)					Extraction (%)
		Ni	Co	Fe	U	^{226}Ra	^{226}Ra
10% ADNNSA + 15% LIX 63	0.98	0.69	0.036	1.69	<0.01	-	-
10% ADNNSA + 15% LIX 54	1.5	1.60	0.036	1.03	0.0008	1780	69
10% ADNNSA + 15% LIX 65 N	1.5	1.63	0.038	1.69	0.0009	1860	69
10% ADNNSA + 10% LIX 26	1.5	1.98	0.045	1.66	0.0006	355	94
10% ADNNSA + 15% LIX 34	1.5	1.79	0.041	1.74	0.0006	970	84
10% ADNNSA + 15% DS5443	1.5	1.00	0.034	1.74	0.0006	1260	79

Eight successive contacts at a feed pH 1.5 using 10% ADNNSA + 15% LIX 63 with the Key Lake feed at A/O 1/1 indicated a loading of 2.6 g Ni/L, 0.011 g Co/L, 0.75 g Fe/L could be obtained. The results are given in Table 6, indicating the extracted radium was not being rejected from the solvent by successive contacts, and was in fact loading further with the additional stages.

Table 6. Successive Extraction Contacts
(10% ADNNSA + 15% LIX 63)

Contact Number	Raffinate				Loaded Solvent				
	Ni	Co	Fe	^{226}Ra (pCi/L)	Ni	Co	Fe	U	^{226}Ra
1	1.01	0.048	1.87	2330	2.21	0.015	0.59	<0.015	3570
2	1.77	0.046	1.88	3140	2.41	0.011	0.60	<0.015	6330
3	1.97	0.046	1.86	4190	2.45	0.013	0.62	<0.015	8040
4	1.96	0.046	1.91	3930	2.54	0.012	0.67	<0.015	10010
5	2.04	0.047	1.86	3930	2.64	0.012	0.71	<0.015	11980
6	1.99	0.046	1.86	3930	2.60	0.013	0.75	<0.015	13950
7	1.99	0.046	1.86	4200	2.67	0.011	0.74	<0.015	15650
8	1.95	0.045	1.84	4040	2.59	0.011	0.75	<0.015	17510

Scrubbing of a solvent (10% ADNNSA + 10% LIX 63) containing 1.17 g Ni/L, 0.48 g Fe/L, 0.011 g Co/L, and about 2000 pCi ^{226}Ra/L was carried out using 100 g/L NaCl at pH 1.0 (with HCl) solution. The phase ratio was varied and the scrubbing was for 2 minutes at room temperature. The results in Table 7 indicate that NaCl will remove ^{226}Ra and would require several stages at high A/O ratios to be effective.

Table 7. Scrubbing of Loaded Solvent with 100 g/L NaCl (pH 1.0)
(10% ADNNSA + 10% LIX 63)

O/A Ratio	Scrub Liquor			
	Ni (g/L)	Fe (g/L)	Co (g/L)	^{226}Ra (pCi/L)
1/10	0.015	0.24	0.011	165
1/2	0.098	0.26	0.011	652
1/1	0.19	0.28	0.011	988
3/1	0.42	0.33	0.011	1890
10/1	0.81	0.38	0.011	2840

Kinetic tests, from 10 seconds to 60 minutes were performed to determine whether any selectivity of nickel extraction over radium would result. The data in Table 8 using 10% ADNNSA + 15% LIX 63 in contact with a

feed adjusted to pH 1.5 with NH_4OH at A/O = 1/1 indicates that rate of extraction did not seem to affect the Ni/Ra ratio in the loaded solvent. This test was not conclusive because the phase separations were much longer than the shorter shaking times and additional extraction may have taken place allowing all elements to attain equilibrium.

Table 8. Effect of Contact Time on Extraction

Time (s)	Loaded Solvent			
	Ni	Fe	^{226}Ra (pCi/L)	Ni/Ra Ratio
10	1.31	0.53	2770	4.7×10^{-4}
30	1.27	0.58	2780	4.6
60	0.77	1.03	2350	3.3
120	1.04	0.67	3170	3.3
180	1.48	0.53	2970	5.0
600	1.42	0.48	3500	4.1
1800	1.44	0.70	4100	3.5
3600	1.17	0.87	3880	3.0

Various concentration mixtures of ADNNSA - LIX 63 were investigated for possible discrimination of Ni over Ra. A phase ratio of A/O 1.5/1, was used and the contact was for 2 minutes at room temperature. The results in Table 9 indicate that a solvent mixture of 5% ADNNSA + 20% LIX 63 provides the highest Ni loading in a single stage together with maximum discrimination over Co and Fe. The ^{226}Ra extracted was less than some of the mixtures, but nevertheless too high (considering it may be difficult to selectively scrub, based on scrub data).

Table 9. Effect of Extractant Mixtures

ADNNSA	LIX 63	Loaded Solvent (g/L)				
		Ni	Co	Fe	U	^{226}Ra (pCi/L)
0	30	<0.004	<0.005	0.018	<0.15	495
2.5	25	0.27	0.044	0.93	<0.15	2070
5	20	1.86	0.008	0.34	<0.15	2080
7.5	15	0.53	0.07	1.94	<0.15	1350
10	10	1.45	0.016	0.74	<0.15	5970
10	15	1.52	0.014	0.72	<0.15	5115
12.5	5	0.93	0.016	0.67	<0.15	4965
15	0	0.94	0.025	1.10	<0.15	65,385

Stripping tests were carried out on the solvent mixture to determine whether any Ni/Ra selectivity would result. Various possible stripping reagents were investigated. The following tests were not analyzed as it was evident by the strip solution color that very little nickel was stripped:

1.0M $(NH_4)_2SO_4$ (pH 0.5)	1.0M NH_4Cl
3.0M H_2SO_4	5% NH_4HF
3.0M HCl	5% ammonium citrate
	5% NH_4NO_3

The stripping with $(NH_4)_2CO_3$ however was somewhat effective for Ni, with 0.5M concentration showing the most promise compared with 1.0M and 1.5M.

3.4 Conclusions on Solvent Extraction

Because of the high co-extraction of ^{226}Ra, and inability to selectively scrub or selectively strip either the Ni or ^{226}Ra, the final Ni product would contain substantial amounts of ^{226}Ra. Therefore no further investigations using solvent extraction were carried out.

In order for solvent extraction to be used successfully another reagent must be found or there would be a requirement for a prior or post precipitation for the removal of radium before a final stage sulphide precipitation of a nickel product. Therefore if a product could be produced by a 2-stage precipitation process the capital and operating costs would be decreased compared with the solvent extraction plus two precipitation circuits. Subsequent tests were therefore performed to determine the viability of precipitation.

4. Precipitation

Precipitation of NiS from similar types of solutions to the Key Lake raffinate have been studied by workers at AMAX (2) and they have developed a successful pilot-scale process.

4.1 Initial Tests on Synthetic Solution

Prior to receiving the shipment of Key Lake raffinate, precipitation tests were performed on a synthetic solution using sodium sulphide (Na_2S). These results, shown in Table 10, indicate that most of the ^{226}Ra present in the solution is co-precipitated with nickel in the pH range 3-4.

Washing tests were performed using 100 g/L of NaCl to determine whether Ra^{226} could be effectively removed from the NiS precipitate. The results indicated that a brine wash is moderately effective in a single stage, but such a procedure may require multiple wash stages. The degree of effectiveness depended strongly on the pH used during precipitation and the wash was poorest where Ni precipitation was most complete.

Table 10. Precipitation with Na_2S

Feed pH	Filtrate after Na_2S	
	Ni (g/L)	^{226}Ra (pCi/L)
Feed	2.00	1140
1.0	1.86	429
2.0	1.49	224
3.0	0.61	386
4.0	0.048	<4
5.0	0.21	<4
6.0	0.34	191

4.2 Tests on Key Lake Raffinate - $CaCO_3$ + Na_2S

Subsequent precipitation tests were performed on the Key Lake raffinate feed solution. The previous tests on the synthetic feed solution of direct sulphide precipitation indicated pH 3-4 as the range for recovery of nickel. Because the radium was also co-precipitated, there would be a requirement for a two-stage precipitation if a radium free nickel sulphide product were to be produced. The feed solution contains iron and arsenic which can co-precipitate with radium. Therefore the raffinate feed solution was adjusted from pH 1.0 to pH 3.5, using limestone at ambient temperature ($CaCO_3$) in order to determine whether the co-precipitation of ferric arsenate plus radium would occur to a useful degree. This reagent was selected because of the better pH control compared to the use of lime. The data in Table 11 indicate that no loss of nickel occurred in this precipitation and that 75% of the ^{226}Ra was precipitated together with most of the U, 54% Al, and 65% Si. However, only 33% of the Fe was precipitated, due to the presence of ferrous iron. Although no As was determined, it would be expected to be relatively high due to the incomplete iron

precipitation. The subsequent Na_2S addition to this filtrate indicated good recovery of nickel but contained 50 pCi/g co-precipitated radium which was a significant improvement. Washing of the sulphide product with 100 g/L NaCl solution was not effective in reducing the radium content. The nickel grade in the product was 12.5% Ni. Substantial co-precipitated iron together with Mg, Si and Al accounted for 20%.

Table 11. $CaCO_3$-Na_2S Precipitation of Key Lake Raffinate (No pre-oxidation)

	Feed Raffinate g/L	After $CaCO_3$ g/L	% Removed %	$CaCO_3$ Precipitate wt %	After Na_2S g/L	% Removed %	Na_2S Precipitate* wt %
Ni	2.06	2.08	0	0.092	0.0008	≈100	12.5
Co	0.047	0.052	0	0.04	<0.0001	≈100	0.31
Fe_t	2.12	1.42	33	1.3	0.0001	≈100	10.0
Fe^{2+}	1.54	1.36	12	-	-	-	-
^{226}Ra	5460	1350	75	131	171	87	52
U	0.0007	<0.0001	≈100	0.0016	<0.0001	-	0.0006
As	1.8	-	-	2.5	-	-	1.6
Mg	0.71	0.73	0	0.05	0.35	52	2.4
Ca	0.67	0.54	19	27.0	0.42	22	0.63
Al	1.08	0.49	55	1.2	<0.001	≈100	3.3
Si	0.41	0.14	66	0.19	<0.001	≈100	4.8
LOI	-	-	-	8.8	-	-	19.8
H_2O	-	-	-	62	-	-	63
pH	0.8	3.41	-	-	10.5	-	-

^{226}Ra in pCi/L or pCi/g
% removed based on solution assays only
*after 6 successive washes with 100 g/L NaCl

4.3 Oxidation of Fe^{2+} to Fe^{3+} Followed by $CaCO_3$ and Na_2S Precipitation

The next series of tests were concerned with the oxidation of Fe^{2+} to Fe^{3+} prior to the limestone addition stage, in order to provide for maximum iron removal prior to the sulphide precipitation step. The feed raffinate solution had an emf of 385 mV. Sparging with either air or the addition of

sodium chlorate had no effect on the oxidation potential due to the fact that a somewhat higher pH (6-8) is usually required for such oxidants as air. However, the addition of excess hydrogen peroxide resulted in the oxidation occurring, with the final emf being 620 mV. The subsequent precipitation with $CaCO_3$ addition to pH 3.5 resulted in essentially complete precipitation of iron and arsenic and increased precipitation of silica (Table 12). Oxidant was added to the 1L batch of feed over a 90 minute period. The $CaCO_3$ addition conditions were not monitored in this first test. Radium removal at 76% was almost the same as shown in the previous table.

4.4 Oxidation - $CaCO_3$-$BaCl_2$-Na_2S Precipitation

Instead of 30% H_2O_2 as an oxidant, an excess amount of Na_2O_2 was used to see if these reagents were equally effective so that any cost advantage of one over the other could be utilized. The pH was raised to pH 3.5 with $CaCO_3$, followed by the addition of $BaCl_2$ to precipitate the radium, prior to Na_2S precipitation. As with the H_2O_2 oxidation, the emf rose to above 625 mV, and the Fe^{2+} was completely oxidized. The results in Table 13 also indicate that the $BaCl_2$ treatment together with the $CaCO_3$ precipitation was an effective means of co-precipitating the $BaRaSO_4$ together with the Fe-As precipitate. The grade of product analyzed 18.1% Ni containing only 2 pCi/g Ra^{226} which is probably an acceptable level. Also, there was 1.6% As which may be satisfactory in the feed to any subsequent refining operation. Other impurities such as Ca, Mg, Si, Al would probably not constitute a problem in the further processing for Ni recovery. The final precipitate was washed with water and with 100 g/L $CaCl_2$ solution but these washes did not improve the product purity.

A similar test was carried out on a 6 litre volume of raffinate feed, in which, following oxidation and $CaCO_3$ + $BaCl_2$ precipitation, the filtrate was split into 5 1-litre portions to investigate the Na_2S requirements at 1, 2, 3, 4, 5 times stoichiometry. The precipitate filter lots were washed with 100 mL water followed by 100 mL of 100 g/L $CaCl_2$ solution. The results indicate that 3X stoichiometric Na_2S is required for maximum nickel precipitation. However, the requirement was probably somewhat high due to poor oxidation-precipitation and thus more iron and other sulphide-consuming contaminants were present than in the previous tests. Satisfactory radium levels of less than 15 pCi/gm were readily obtained.

In both tests the oxidant was added progressively over a period of approximately 3 hours with agitation. The solution was allowed to stand overnight. The $CaCO_3$ precipitation was carried out in a similar fashion with progressive addition of the reagent over a 4 hour period. The $BaCl_2$ (4 g/L) was added in one lot to the solution before the $CaCO_3$ was filtered out but after the pH had been raised. The solution was stirred for 45 minutes and 20 hours with samples at each time. Na_2S was also added in one lot, stirred for 1 hour and then the precipitate was separated. Any washes of the cakes were done by repulping for 20 minutes and then filtering.

Table 12. Oxidation - $CaCO_3$-Na_2S Precipitation of Key Lake Raffinate

	Feed Raffinate g/L	After H_2O_2 and $CaCO_3$ g/L	% Removed %	$CaCO_3$ Precipitate wt %	After Na_2S g/L	% Removed %
Ni	2.04	2.14	0	0.22	0.37	83
Co	0.045	0.048	0	0.011	<0.01	>80
Fe_t	2.02	0.004	99.8	4.8	<0.02	-
^{226}Ra	4880	1150	76	82	145	87
U	0.0007	0.0003	60	0.0012	0.0031	?
As	1.8	-	-	4.0	-	-
Mg	0.66	0.68	0	0.08	0.69	0
Ca	0.66	0.54	18	22.7	0.50	7
Al	1.17	0.85	27	0.76	<0.001	~100
Sr	0.42	0.080	81	0.61	0.039	51
Na	0.029	0.023	21	-	4.06	-
LOI	-	-	-	15.6	-	-
H_2O	-	-	-	65	-	-
pH	0.68	3.5	-	-	-	-
emf	392	620	-	-	-	-

^{226}Ra in pCi/L or pCi/g
% removed based on solution assays only

Table 13. Oxidation - $CaCO_3$ + $BaCl_2$ - Na_2S Precipitation

	Feed Raffinate g/L	After Na_2O_2 g/L	After $CaCO_3$ g/L	After $BaCl_2$ (45 m) g/L	After $BaCl_2$ (20 h) g/L	% Removed %	$BaCl_2$-$CaCO_3$ Precipitate wt %	After Na_2S g/L	% Removed %	Na_2S^+ Precipitate wt %
Ni	2.39	2.56	2.46	2.34	2.38	≈ 0	0.18	<0.009	≈100	18.1
Co	0.054	0.056	0.047	0.051	0.044	≈ 19	0.006	<0.011	≈100	0.50
Fe_t	2.05	2.03	0.006	0.005	0.004	≈100	5.7	0.0002	-	0.7
Fe^{2+}	1.46	0.004	0.0006	0.0007	0.0004	≈100	-	<0.0001	-	-
^{226}Ra	5990	5720	1400	-	-	99+*	122	<40	-	2
U	0.0013	0.0010	0.0004	0.0010	0.011	15	0.0015	0.0010	10	0.0033
As	1.84	1.86	<0.001	0.002	<0.001	≈100	6.4	<0.001	-	0.4
Zr	0.001	0.001	0.001	0.0006	0.0007	30	-	<0.0001	≈100	0.003
Mg	0.71	0.72	0.73	0.75	0.79	≈ 0	0.065	0.62	22	1.32
Ca	0.68	0.66	0.55	0.50	0.47	31	21.1	0.42	11	0.35
Al	1.18	1.18	1.07	1.09	1.17	≈ 0	0.39	<0.001	≈100	9.01
Si	0.44	0.47	0.15	0.11	0.096	78	0.76	0.064	33	-
LOI	-	-	-	-	-	-	15.3	-	-	36.9
H_2O	-	-	-	-	-	-	55	-	-	63
pH	0.9	1.1	3.54	-	-	-	-	-	-	-
emf	370	670	490	-	-	-	-	-	-	-

^{226}Ra in pCi/L or pCi/g
% removed based on solution assays
*estimated
+after single water wash + single $CaCl_2$ (100 g/L) wash

4.5 Oxidation - $CaCO_3$ Precipitation - Ion Exchange Removal of Radium

The oxidation - $CaCO_3$ precipitation process seems to be effective for the co-precipitation of most of the impurities that would ordinarily report in the NiS precipitate. This stage is considered to be readily able to be incorporated in the Key Lake mill. $BaCl_2$ is used in the process, as is also ion exchange for the final polishing stage for radium removal. Therefore, a test was performed to determine the effectiveness of an oxidation - $CaCO_3$ precipitation-ion exchange treatment. The oxidation with Na_2O_2 was effective and the $CaCO_3$ addition to pH 3.5 resulted in a filter cake that filtered well. Following filtration, the filtrate was contacted in two ion exchange column tests in which Dow XFS radium selective resin was compared with natural barite sorption. The results indicated that the Dow XFS resin was somewhat less effective than the barite (which had a smaller particle size and so more available surface which may account for the effectiveness). The Dow XFS resin showed 200 pCi/L after 4 hours and the concentration leveled off after 48 hours of 70 pCi/L. By contrast the barite leveled off at <40 pCi/L ^{226}Ra after 4 hours. The ion exchange results are shown in Fig. 2 and the pre-treatment oxidation-precipitation data are summarized in in Table 14. No precipitation of NiS was carried out on the solutions examined in these tests.

For the solution, the treatment was similar to the feeds described above. Oxidation was carried out over a period of 90 minutes. The $CaCO_3$ addition took 90 minutes as well and was filtered after this time. The solution was then submitted for the radium removal treatments which took place some days later.

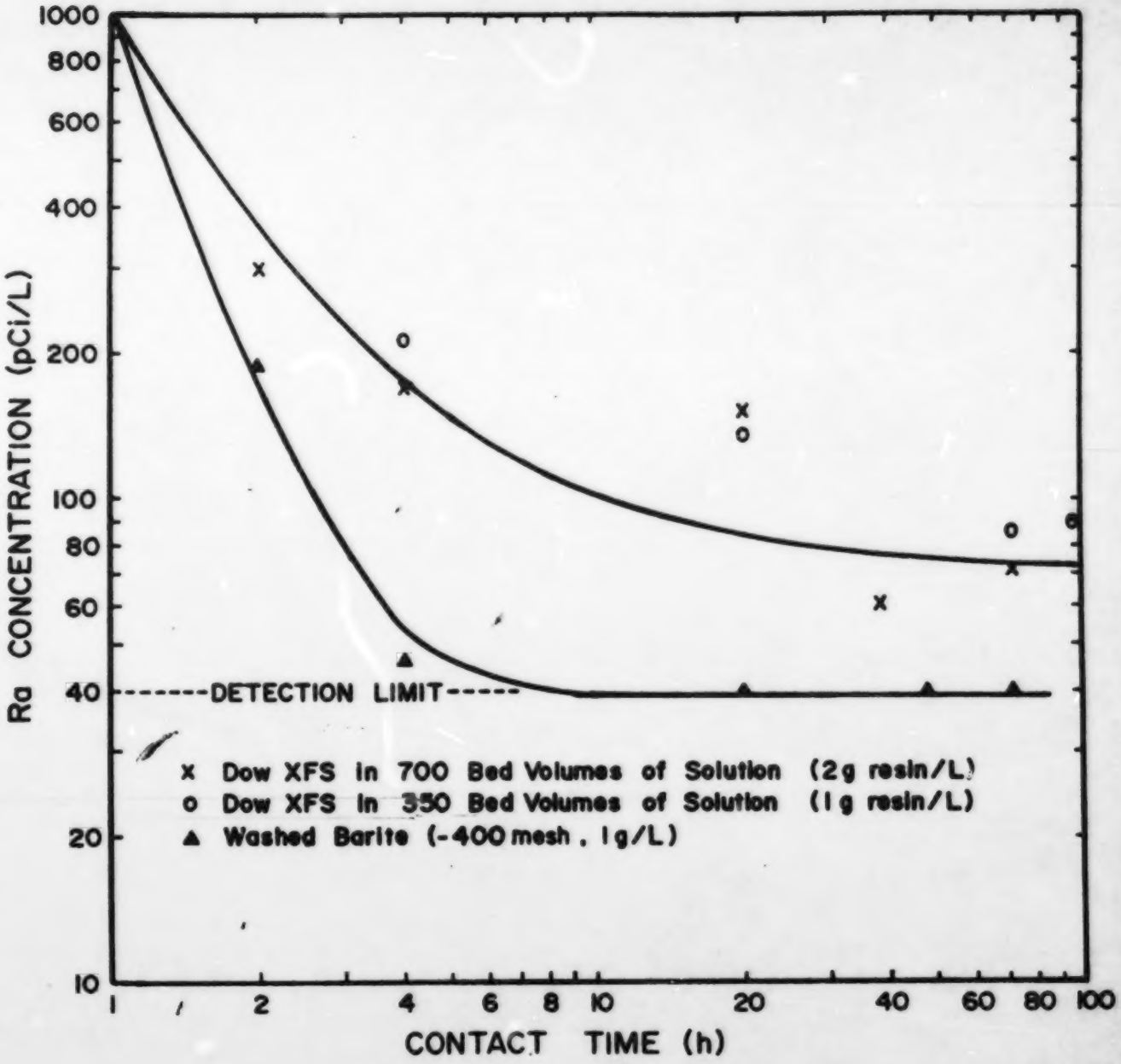

Fig. 2 Radium removal with Barite or by IX

Table 14. Oxidation - $CaCO_3$ Pretreatment before IX or Barite Removal of Ra

	Feed Raffinate g/L	After Na_2O_2 g/L	After $CaCO_3$ g/L	% Removed %	$CaCO_3$ Precipitate wt %
Ni	2.04	2.04	2.11	≈0	0.36
Co	0.044	0.045	0.044	≈0	0.01
Fe_t	2.02	2.07	0.013	99+	5.01
Fe^{2+}	1.30	0.026	0.004	99+	-
^{226}Ra	5200	5270	1200	87	113
U	0.0009	0.0006	0.0003	67	0.0012
As	1.74	1.78	<0.001	≈100	5.7
Zr	0.0009	0.0009	0.0007	22	0.005
Mg	0.71	0.71	0.69	3	0.07
Ca	0.65	0.66	0.48	26	5.35
Al	1.04	1.04	-	≈0	0.27
Si	0.39	0.44	0.30	23	0.83
Na	-	-	-	-	0.29
LOI	-	-	-	-	14.9
H_2O	-	-	-	-	57
pH	0.9	1.01	3.51	-	-
emf	390	670	425	-	-

^{226}Ra in pCi/L or pCi/g
% removed based on solution assays

5. Reagent Selection and Costs

It is possible from the data which has been obtained to date to make a reasonable estimate of the cost of the reagents required to produce the NiS product. Cost estimates have been made on the basis of the reagent required to produce final precipitate containing 1 kg of Ni. With the feed solution at 2.1 g Ni/L and assuming a conservative value of 95% for the recovery of Ni, a total of 500 L of feed are required to produce the 1 kg Ni containing precipitate.

Costs have been calculated only for the reagents additional to what is currently used in the Key Lake mill. It is assumed that the same quantities of CaO (or equivalent $CaCO_3$ which may be less costly) and the same amount of $BaCl_2$ would be used as is currently needed to treat the raffinate before it can be pumped to the tailings impoundment.

For oxidant, tests have been carried out using both sodium peroxide and hydrogen peroxide. The sodium reagent appeared to be more effective in that half the weight was required to produce the same rise in the solution emf. Furthermore, the Na reagent raises the pH of the solution slightly which is desirable. However, the cost of the Na_2O_2 is prohibitive and the reagent is not readily available in bulk. Typical prices fob Toronto or Ontario are:

Na_2O_2 = \$100/kg = \$16.40/mole of O_2 released.

H_2O_2 = \$1/kg (50% reagent) = 15.2 /mole of O_2 released

Using H_2O_2, we require = 1.5 g/L of feed x 500L x\$1/kg
= \$0.75/kg Ni for oxidant.

Sodium sulphide was used for the precipitation of the final product. The chemical used in the laboratory is $Na_2S.9H_2O$ which is the reagent grade material obtained by recrystallization. Na_2S is available in technical grades as bagged flake which is 60% active reagent. The cost of this reagent is typically \$0.80/kg fob Toronto. There may well be local supplies closer to Saskatoon from the fertilizer industry. In the laboratory it was difficult to determine the exact quantity of Na_2S required because the recrystallized product is extremely deliquescent and dry crystal could not be obtained. However, the data does indicate that using 1.5 mole of Na_2S for each mole of Ni should be sufficient to give complete precipitation. This represents a cost of 1000 g Ni/58.7g/mole x 1.5 mole Na_2S/mole Ni x 78g/mole x 1/0.6 (active reagent) x \$0.80/kg = \$2.70/kg Ni for oxidant.

Therefore, total additional reagent cost amounts to \$3.45 (kg contained Ni). Taking the price of Ni at about \$3/lb or \$6.60/kg leaves \$3.15 to cover additional capital costs for the plant and other operating costs such as labour and maintenance. Additional maintenance costs over the current precipitation plant should not be large although the introduction of filters in two steps may add costs. It should also be possible to operate with no more than 1 person year to look after this precipitation circuit. Capital costs are difficult to estimate and would require a more thorough engineering study.

Finally, there may exist opportunities to significantly reduce some of the additional reagent costs. For the oxidant, attempts were made to use oxygen which is already available in the plant, either alone or in combination with peroxide. This work was not successful in the pH range up to pH = 5. The peroxide requirement has not been optimized yet. A decision should also be made as to whether the oxidation step should be omitted altogether. Without oxidation, the final product contains Fe and As impurity. There may also be a penalty in increased sulphide consumption by Fe and As. If the smelting charge penalty and the increased sulphide cost amount to less than $0.75/kg Ni produced it is worth eliminating the oxidation step altogether. A substitute for Na_2S may be available in NaHS, the hydrosulfide which is already used in western Canada for the separation of Mo from Cu by precipitation. This reagent was quoted to cost $0.72 /kg on a 100% active basis and it is supplied as an aqueous solution with a strength of 45-47%. Being a liquid may also make handling easier. Using the $0.72 value substituting mole for mole for Na_2S gives a precipitant cost of $1.03/kg Ni which is a very significant reduction. Additional testing will show whether this material can be used in the flowsheet.

The use of H_2S instead of Na_2S may also be worth investigating although there would be additional handling costs with H_2S which may cancel out any cost savings.

6. Discussion and Conclusions

Nickel can be easily recovered from the Key Lake uranium process raffinate, but recovery is not really the problem. Solvent extraction was considered as the ideal method of separation and recovery of nickel from the solution, and technology was available based on previous work at CANMET and elsewhere. However, radium was co-extracted generally to the same extent as nickel. Co-extraction of radium was high, whether extracting at an equilibrium pH 5 or pH 1.5 using DEHPA + TBP or ADNNSA + LIX 63 respectively. Although a scrub with NaCl solution was moderately effective for removing radium preferentially to nickel, it could be costly because of the number of stages and high A/O ratios required. Stripping of the solvents for recovery of nickel was not without difficulty in the case of the ADNNSA and further work would be required. Because of the problem of radium co-extraction and the difficulty of providing a suitable strip

solution to sulphide precipitation of a nickel product free of radium, the idea of using solvent extraction was dropped.

Because of the problem of radium following the nickel in the sulphide precipitation it was concluded that the prior precipitation would be necessary to remove radium as well as other contaminants that would ultimately report in a sulphide product. To this end precipitation tests were carried out. Data indicated that controlled emf oxidation of the Fe^{2+} to Fe^{3+} to about 600-650 mV with H_2O_2 or Na_2O_2 prior to neutralization with $CaCO_3$ to precipitate essentially all the Fe and As was effective. The levels of other impurities such as Al, Ca, Si and Mg were reduced to various degrees. Incorporation of $BaCl_2$ addition to the precipitation stage also resulted in the co-precipitation of $BaRaSO_4$.

The filtrate from the oxidation-precipitation stage was treated with Na_2S to precipitate the NiS product. Such a combined treatment resulted in a grade of 18% Ni containing 2 pCi/g Ra^{226}. This could probably be considered a suitable product feed to subsequent refining.

An alternative purification route consisted of a similar oxidation-precipitation followed by ion exchange removal of the radium. This was also very successful. The alternatives are shown in Fig. 3.

The following conclusions can be drawn from the research:

1) solvent extraction using presently available extractants does not appear to be a technical or economic possibility in achieving a suitable radium free product;

2) oxidation-precipitation with $CaCO_3$ and $BaCl_2$ is effective in co-precipitating Fe, As, Ra;

3) oxidation-precipitation with $CaCO_3$ followed by ion exchange removal of radium is also effective for removing all the above contaminants; and

4) sodium sulphide addition to the purified filtrate results in a product of about 18% Ni, 0.5% Co grade containing about 2 pCi/g Ra^{226}.

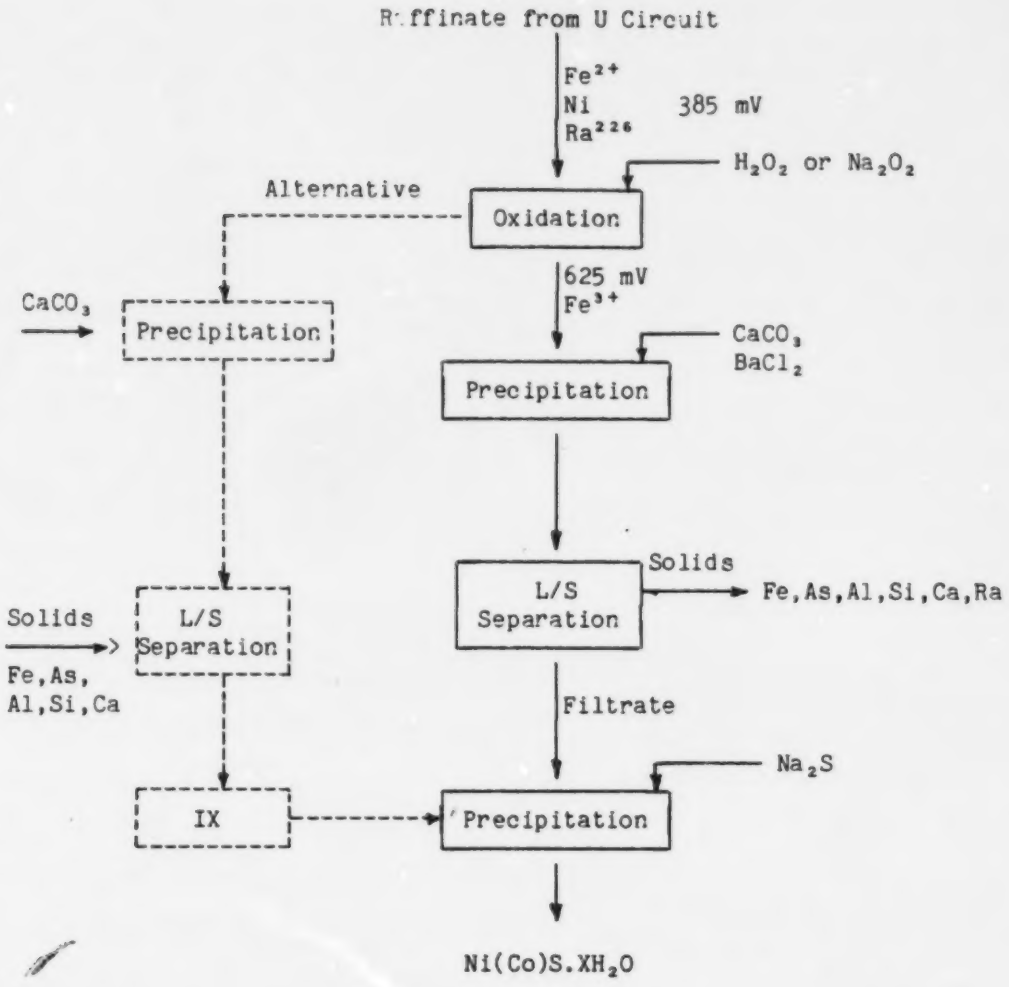

Fig. 3. Possible Nickel (Cobalt) Recovery Process from Key Lake Uranium Process Raffinate

7. Recommendations

The data accumulated on this project indicates that a process to recover nickel from the Key Lake uranium process raffinate is feasible. However, it must be demonstrated on a larger scale in order to produce a quantity of nickel sulphide product sufficient to be evaluated by potential buyers. An order of magnitude of several kilograms is suggested as the amount to produce. Possible customers for such a product would include Sherritt-Gordon, Falconbridge at Kristiansand, Nippon Mining and Sumitomo Metal Mining.

Further work is required to establish the precipitation conditions. The experiments to date have focussed primarily on the chemistry of the precipitation step. The degree of agitation required, methods of addition, length of time needed in each step and the actual quantities of each reagent all need to be fixed.

8. Acknowledgement

The authors would like to thank V.M. McNamara and L.E. Carter of the Solution Purification Section for setting up and carrying out the ion exchange tests and J.L. Dalton for prompt Ra analysis and advice.

9. References

1. G.M. Ritcey, A.W. Ashbrook, Solvent Extraction Principles and Applications to Process Metallurgy, Part II. Elsevier Publishing Co., New York, 1979.

2. M. Jha, G. Meyer, G. Wicker, J of Metal Nov. 1981, pg. 48-53.